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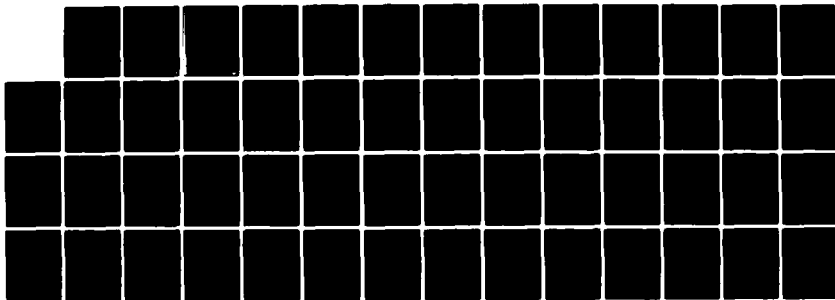
THE REACTION CHEMISTRY OF TRANSITION METAL
DIPHENYLPHOSPHORUS COMPLEXES W. (U) STATE UNIV OF NEW
YORK AT BUFFALO DEPT OF CHEMISTRY
C TESSIER-YOUNGS ET AL. 28 MAR 83

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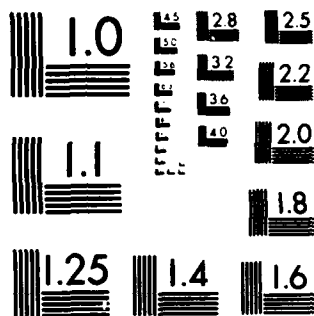
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retain their identity as cyclic ethers. Subsequent reactions of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K} \cdot 2(\text{dioxane})$ with AlR_2Br ($\text{R} = \text{Br}, \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$) in THF lead to the formation of high yields of fully characterized compounds with the empirical formula $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{AlR}_2]$. The $(\text{CH}_2)_4\text{O}$ unit arises from the cleavage of a THF molecule. No THF-aluminum adducts are observed. The compound $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{Al}(\text{CH}_2\text{SiMe}_3)_2]$ which incorporates a new amphoteric ligand has also been characterized by an x-ray structural study. The crystal is composed of dimeric units of formula $[\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{Al}(\text{CH}_2\text{SiMe}_3)_2]]_2$ which are in the centrosymmetric monoclinic space group $\text{P2}_1/\text{n}$ with $a = 11.939(3)\text{\AA}$, $b = 14.940(\text{\AA})$, $c = 21.014(5)\text{\AA}$, $\beta = 102.88(2)^\circ$, $V = 3654\text{\AA}^3$, $Z = 2$ (dimeric units) and mol wt 1301.5. Diffraction data ($2\theta(\text{max}) = 35^\circ$, MoK α radiation) were collected with a Syntex P2_1 automated four-circle diffractometer, the structure was solved by Patterson and difference-Fourier techniques, and the model refined to $R_F = 9.2\%$ and $R_{\text{WF}} = 8.2\%$ for 1515 reflections with $|F_o| > 3\sigma(|F_o|)$. The dimeric molecule lies on an inversion center. Each octahedral $(\text{OC})_5\text{CrPPh}_2$ - fragment is linked by an $-(\text{CH}_2)_4\text{O}-$ unit (formed by cleavage of THF) to the two $\text{Al}(\text{CH}_2\text{SiMe}_3)_2$ fragments. The central Al-O-Al-O ring is strictly planar, with obtuse Al-O-Al angles of $100.3(6)^\circ$ and acute O-Al-O angles of $79.7(5)^\circ$. The second route to chromium derivatives of amphoteric aluminum-phosphorus ligands, small molecule elimination reactions between $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and AlMe_3 or AlMe_2H , does not lead to compounds with Cr-P-Al bonds. Our observations suggest that the major site of reaction for the aluminum compounds is the carbonyl ligand.

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The Reaction Chemistry of Transition Metal Diphenylphosphorus Complexes with Organoaluminum Compounds. The Synthesis, Characterization and Crystal and Molecular Structure of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$, An Example of THF Cleavage

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[Contribution from the Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York 14214]

The Reaction Chemistry of Transition Metal Diphenylphosphorus
Complexes with Organoaluminum Compounds. The Synthesis,
Characterization and Crystal and Molecular Structure of
 $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$. An Example of THF Cleavage

by

C. Tessier-Youngs, Wiley J. Youngs, O. T. Beachley, Jr.* and
Melvyn Rowen Churchill*

Abstract

Metathetical and small molecule elimination reactions between appropriate transition metal carbonyl diphenylphosphorus complexes and organoaluminum compounds have been investigated as synthetic routes to transition metal derivatives of amphoteric ligands. The synthesis, characterization and properties of the starting compounds for the metathetical reactions, $\text{M}(\text{CO})_5\text{PPh}_2 \cdot n(\text{dioxane})$ $\text{M} = \text{Cr}, \text{W}$, $n=2$; Mo , $n=1$ from $\text{M}(\text{CO})_5\text{PPh}_2\text{H}$ and KH is described. All data confirm that the dioxane molecules in these complexes retain their identity as cyclic ethers. Subsequent reactions of $\text{Cr}(\text{CO})_5\text{PPh}_2 \cdot 2(\text{dioxane})$ with AlR_2Br ($\text{R} = \text{Br}, \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$) in THF lead to the formation of high

yields of fully characterized compounds with the empirical formula $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$. The $(\text{CH}_2)_4\text{O}$ unit arises from the cleavage of a THF molecule. No THF-aluminum adducts are observed. The compound $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$ which incorporates a new amphoteric ligand has also been characterized by an x-ray structural study. The crystal is composed of dimeric units of formula $[\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]]_2$ which are in the centrosymmetric monoclinic space group $\text{P}2_1/\text{n}$ with $a = 11.939(3)\text{\AA}$, $b = 14.940(\text{\AA})$, $c = 21.014(5)\text{\AA}$, $\beta = 102.88(2)^\circ$, $V = 3654 \text{\AA}^3$, $Z = 2$ (dimeric units) and mol wt 1301.5. Diffraction data ($2\theta(\text{max}) = 35^\circ$, $\text{MoK}\alpha$ radiation) were collected with a Syntex $\text{P}2_1$ automated four-circle diffractometer, the structure was solved by Patterson and difference-Fourier techniques, and the model refined to $R_F = 9.2\%$ and $R_{\text{WF}} = 8.2\%$ for 1515 reflections with $|F_o| > 3\sigma(|F_o|)$. The dimeric molecule lies on an inversion center. Each octahedral $(\text{OC})_5\text{CrPPh}_2$ - fragment is linked by an $-(\text{CH}_2)_4\text{O}-$ unit (formed by cleavage of THF) to the two $\text{Al}(\text{CH}_2\text{SiMe}_3)_2$ fragments. The central Al-O-Al-O ring is strictly planar, with obtuse Al-O-Al angles of $100.3(6)^\circ$ and acute O-Al-O angles of $79.7(5)^\circ$. The second route to chromium derivatives of amphoteric aluminum-phosphorus ligands, small molecule elimination reactions between $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and AlMe_3 or AlMe_2H , does not lead to compounds with Cr-P-Al bonds. Our observations suggest that the major site of reaction for the aluminum compounds is the carbonyl ligand.

Introduction

The new compound, $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{NMe}_3]$, can be considered to be a transition metal derivative of an amphoteric main-group element ligand.¹ This first example of a compound in which the diphenylphosphido group bridges a transition metal and a main-group metal was readily prepared in high yield by an apparent ligand substitution reaction of $\text{Cr}(\text{CO})_5\text{NMe}_3$ by $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ in benzene solution. An alternate synthetic route to these transition metal derivatives of amphoteric ligands involves starting with a phosphorus derivative of a transition metal complex and then effecting a chemical reaction which would lead to the formation of the desired phosphorus-main group element bond. As part of this research effort we have studied the metathetical reactions of transition metal diphenylphosphide anions with main-group metal halogen compounds as well as attempted small molecule elimination reactions between transition metal diphenylphosphine derivatives and organoaluminum compounds. Both types of reactions might be expected to give the desired compounds with aluminum-phosphorus bonds² but novel observations were made instead.

In this paper, the synthesis and characterization of the precursor compounds, $\text{M}(\text{CO})_5\text{PPh}_2\text{K}\cdot n(\text{ether})$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$) from $\text{M}(\text{CO})_5\text{PPh}_2\text{H}$ and KH are described. These reactions are compared to the related deprotonation reactions using $n\text{-BuLi}$.³ Then, the reactions of the transition metal phosphorus compounds with organoaluminum compounds are discussed. In most cases the synthetic reactions did not lead to a final product with a transition metal-phosphorus-aluminum atom sequence. For example, the reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$

in THF solution leads to the formation in high yield of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$, an example of THF cleavage. This compound which incorporates a new amphoteric ligand has been fully characterized by analysis, spectroscopic methods and an x-ray structural study. The reactions of transition metal phosphorus compounds with other organoaluminum compounds are also considered.

Experimental

All compounds were handled in an inert atmosphere employing vacuum line or dry-box (99.998% Argon) techniques. Ether solvents were dried, stored and vacuum distilled from sodium/benzophenone ketyl. Hydrocarbon solvents were treated with sulfuric acid, dried and stored over sodium and vacuum distilled from P_2O_5 immediately prior to their use. Purification of $AlBr_3$ and $AlMe_3$ consisted of sublimation at 60° or room temperature distillation, respectively, both under high vacuum. The reagent $n-BuLi$ in hexane was standardized using solid diphenylacetic acid.⁴ Gaseous HCl and HBr were fractionated through a -78° into a -196° trap. Potassium and sodium hydride in paraffin oil (Alfa/Ventron) were washed repeatedly with hexane. The compounds Ph_2PH^5 , $Cr(CO)_5PPh_2H^6$, $Mo(CO)_5PPh_2H^6$, $W(CO)_5PPh_2H^6$, $KPPh_2 \cdot 2(\text{dioxane})^7$, $AlMe_2H^8$ and $Al(CH_2SiMe_3)_2Br^9$ were prepared and purified by literature procedures. An exchange reaction between one mole of $AlBr_3$ and two moles of the trialkylaluminum compound was used to prepare $AlMe_2Br$ and $AlEt_2Br$. They were judged pure by comparison of their boiling point, vapor pressure and/or density with literature values.^{10,11} The liquids $AlMe_2Br$ (1.37 g/ml), $AlEt_2Br$ (1.29 g/ml¹¹) and $Al(CH_2SiMe_3)_2Br$ (1.06 g/ml⁹) were measured by volume rather than by weight by using graduated gas-tight syringes in the dry-box.

Spectra. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer and were referenced to polystyrene. Spectra of gases were obtained by means of a 10 cm gas cell equipped with KBr plates. Spectra of solids were observed as Nujol mulls using CsI plates. Nujol mulls of the transition metal phosphido anions retained

their bright orange-yellow color and gave reproducible spectra for about one-half hour. Attempts were made to obtain solution spectra of these complexes. THF solutions were prepared in a dry-box and injected into sealed KBr solution cells. Before the spectrum could be scanned completely, decomposition, as evidenced by a greenish color, occurred. In one run of the spectrum of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$, the decomposition was successfully monitored over a period of 15 min, allowing us to deduce the spectrum of the complex.

^1H NMR spectra were recorded at 60, 90 and 100 MHz using Varian Model T-60, Varian Model EM-390 and Jeolco Model MH-100 spectrometers, respectively and are reported in δ units, downfield from tetramethylsilane. The ^{31}P NMR spectra were recorded at 40.5 MHz by means of a Varian Model XL-100 spectrometer, or at 109.16 MHz by means of a JEOL FX-270 spectrometer and were referenced to 85% H_3PO_4 . Proton decoupled spectra are reported in δ units (+ downfield from H_3PO_4). All NMR tubes were sealed under vacuum.

Molecular Weight Measurements. Cryoscopic molecular weights were determined in benzene solution using an instrument similar to the one described by Shriver.¹² Molecular weights are reported in terms of calculated molality, observed molecular weight and association.

Analyses. Analyses for C, H, and P were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Bromine was determined by a standard gravimetric procedure. The following procedure was used for the determination of hydrolyzable alkanes. Accurately weighed samples were hydrolyzed using water or dilute nitric acid. Methane (-196°) and ethane (78°) were measured using a Toepler pump and gas burette assembly after the hydrolyzed samples were cooled to the required temperature. Tetramethylsilane was separated from the hydrolyzed sample by

fractionation through two Dry Ice/acetone (-78°) and a liquid nitrogen (-196°) traps and measured using a standardized volume of the vacuum line. Gases were identified by vapor pressure measurements of their condensed phases and by infrared spectra.

Synthesis of $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ ($M = Cr, Mo, W$). The compounds of general formula $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ were prepared from the reaction of a slight excess of $M(CO)_5PPh_2H$ with KH in dioxane. The experimental procedure for these reactions was identical for all samples of $M(CO)_5PPh_2H$; therefore, only a typical synthesis of $Cr(CO)_5PPh_2K \cdot 2(\text{dioxane})$ will be described in detail. A 2-neck flask containing 7.979 g (20.95 mmol) $Cr(CO)_5PPh_2H$ was equipped with a side arm dumper containing 0.830 g (20.6 mmol) KH. The reaction vessel was evacuated and 20 mL dioxane was vacuum distilled onto the $Cr(CO)_5PPh_2H$. The KH was slowly added to the stirred pale yellow $Cr(CO)_5PPh_2H$ solution. The KH reacted, as evidenced by vigorous bubbling and the formation of a bright orange-yellow solution. After 1-2 h, a yellow precipitate formed. The mixture was stirred for about 24 h, until evolution of hydrogen (typically over 95%) had ceased. Hexane (20 mL) was vacuum distilled into the flask to completely precipitate the yellow solid. The dioxane/hexane solution was separated from the solid by filtration. Then the solid was dried at room temperature under high vacuum for 12 h. It is important not to heat the solid during the drying process as irreversible decomposition takes place (see melting points). The complex $Cr(CO)_5PPh_2K \cdot 2(\text{dioxane})$ (11.53 g) was isolated in 94% yield. In general, yields ranged 85-95% for $M(CO)_5PPh_2K \cdot n(\text{dioxane})$. These

bright orange-yellow compounds are insoluble in aliphatic and aromatic hydrocarbons, are very slightly soluble in diethyl ether and dioxane, have good solubility in THF and DME but react with halogenated hydrocarbons.

$\text{Cr}(\text{CO})_5\text{PPh}_2\text{K} \cdot 2(\text{dioxane})$. Mp: irreversible decomposition begins at 45-50°. Anal. Calc.: C, 50.67; H, 4.42; P, 5.21. Found: C, 50.06; H, 4.43; P, 5.42. IR (Nujol mull, cm^{-1}): ν_{CO} 2074(m), 1970(m,sh), 1941(vs), 1906(s,sh); (THF) 2035(m), 1927(vs).

$\text{Mo}(\text{CO})_5\text{PPh}_2\text{K} \cdot \text{dioxane}$. MP: irreversible decomposition begins at 120°. Anal. Calc.: C, 45.99; H, 3.31; P, 5.65. Found: C, 45.91; H, 3.72; P, 5.62. IR (Nujol mull, cm^{-1}): ν_{CO} 2058(vw), 1972(m,sh), 1952(s), 1865(vs), 1823(vs), 1780(s).

$\text{W}(\text{CO})_5\text{PPh}_2\text{K} \cdot 2(\text{dioxane})$. Mp: irreversible decomposition begins at 55-60°. Anal. Calc.: C, 41.45; H, 3.62; P, 4.78. Found: C, 41.73; H, 3.34; P, 4.74. IR (Nujol mull, cm^{-1}): ν_{CO} 2059(w), 1972(m,sh), 1935(vs), 1896(m).

Reaction of $\text{M}(\text{CO})_5\text{PPh}_2\text{H}$ with KH in THF. The solvent THF was also a useful solvent for the deprotonation of $\text{M}(\text{CO})_5\text{PPh}_2\text{H}$ by KH. The experimental procedure was identical to that used with dioxane and the evolution of H_2 was greater than 95%. However, the products usually came out of solution as viscous oils which eventually solidified upon removal of solvent under high vacuum for several hours. Products from these reactions were not characterized by analysis. The number of bound ether molecules were determined from reactions of the products with anhydrous HCl or HBr (*vide infra*). :

$\text{Cr}(\text{CO})_5\text{PPh}_2\text{K} \cdot \text{THF}$. Mp: irreversible decomposition begins at 55°. IR (Nujol mull, cm^{-1}): ν_{CO} 2046(w), 1988(m,sh), 1938(vs), 1920(vb,s). ^{31}P NMR (THF, ppm from 85% H_3PO_4 , δ) - 21.4(s).

$\text{Mo(CO)}_5\text{PPh}_2\text{K}\cdot 2(\text{THF})$. Mp: irreversible decomposition begins at 125° . IR (Nujol mull, cm^{-1}): ν_{CO} 2038(m), 1970(m,sh), 1930(vs,vb).

Reactions of $\text{M(CO)}_5\text{PPh}_2\text{H}$ ($\text{M} = \text{Cr}, \text{W}$) with NaH. The reaction of $\text{M(CO)}_5\text{PPh}_2\text{H}$ with NaH was much slower than the analogous KH reaction. At least one week was required for complete reaction at room temperature in dioxane. Moderate yields of sodium salts were obtained by refluxing a slight deficiency of NaH with a THF or dioxane solution of $\text{M(CO)}_5\text{PPh}_2\text{H}$ for 6-8 h. Longer reflux times resulted in the formation of undesirable red products. These transition metal phosphide anions were also characterized by their reaction with HBr. (*vide infra*). However, due to the low solubility of the sodium complexes and NaH in these solvents, it was not possible to quantitatively separate these compounds.

Characterization of Deprotonated Complexes by Reaction with HCl or HBr. A weighed sample of the complex was placed in a reaction bulb with an NMR tube side arm. Deuterated toluene or benzene followed by a slight excess of HX were vacuum distilled into the reaction vessel. The insoluble, brightly colored $\text{M(CO)}_5\text{PPh}_2\text{M}_1\cdot n(\text{ether})$ ($\text{M}_1 = \text{Li}, \text{Na}, \text{K}$) completely reacted with HX in less than 8 h, producing a pale yellow or pale orange solution and a white precipitate. The solution was poured into the NMR tube side arm, a TMS marker was added by vacuum distillation, then the tube was sealed and the ^1H NMR spectrum was recorded using a Jeolco Model MH 100 spectrometer. In all cases, the only signals observed were those expected for $\text{M(CO)}_5\text{PPh}_2\text{H}$, the ether, TMS and the residual protons from the deuterated solvent. Due to the presence of these residual protons

from the deuterated solvent, estimates of the number of ether molecules had to be obtained from the integration of the relatively weak P-H signal with respect to the ether signals. The above procedure was used to check the integrity of samples stored in the dry-box for prolonged periods. Some samples were observed to be stable to storage for over a year.

In a similar manner, deprotonated complexes were reacted with HCl or HBr in ether solvents. The infrared spectra of the resulting solutions showed only the simple spectra of $M(CO)_5PPh_2H$.

Reactions of $Cr(CO)_5PPh_2H$ with $n-BuLi$ in Hexane. A solution of 1.019 g (2.694 mmol) $Cr(CO)_5PPh_2H$ in 25 mL hexane was prepared in a 2-neck flask on the vacuum line. Standardized Li n-Bu solution (1.10 mL, 2.39 M, 2.63 mmol) was slowly added to the stirred $Cr(CO)_5PPh_2H$ by means of an addition tube. The pale yellow solution clarified and a mustard-yellow solid formed initially. Within a few minutes, a small amount of a brown solid also formed as a crust over the yellow solid. The precipitates were washed with hexane several times and in the dry box the majority of the brown materials were manually removed from the mustard-yellow powder (0.890 g). Mp: slow decomposition begins at 40° . IR (Nujol mull, cm^{-1}): ν_{CO} 2071(w), 1978(m,sh), 1919(vs), 1873(s,sh) (occasionally a very weak band at 1658 cm^{-1} was also observed). The mustard-yellow powder, presumably $Cr(CO)_5PPh_2Li$, is extremely unstable, slowly decomposing to a brown solid in dry-box atmospheres in which aluminum alkyls are stable. The compound is insoluble in hydrocarbon solvents, soluble in ethers and reacts with halogenated hydrocarbons. The preparative reaction conditions were varied in order to avoid the

formation of the brown solids. Slow addition of the n-BuLi solution gave the least amounts of brown solids. Lowering the reaction temperature, varying the rate of stirring or the reagent concentrations either had no effect or increased the amount of brown materials. Employing an excess of n-BuLi solution gave proportionately larger quantities of the brown solid. Addition of n-BuLi by syringe rather than from an addition tube also increased the amount of brown materials.

Reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and $\text{KPPh}_2 \cdot 2(\text{dioxane})$ in Diethyl Ether.

Diethyl Ether (7 mL) was distilled onto 0.195 g (0.515 mmol) $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and 0.202 (0.504 mmol) $\text{KPPh}_2 \cdot 2(\text{dioxane})$. The pale yellow $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ solution immediately turned to bright yellow as the orange $\text{KPPh}_2 \cdot 2(\text{dioxane})$ crystals gradually disappeared. The solution became cloudy and after stirring overnight a fine yellow precipitate and a yellow solution were present. (Both $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}$ and KPPh_2 are essentially insoluble in Et_2O .) Et_2O was removed by vacuum distillation and the solid was quickly washed with 5 mL hexane. A ^1H NMR spectrum of the sticky yellow hexane soluble residue showed that $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and Ph_2PH were present in a ratio of 4 to 3.

Reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and KPPh_2 in THF. In a separate reaction, 0.328 g (0.867 mmol) $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and 0.914 g (0.866 mmol) KPPh_2 (prepared in Et_2O) were combined in 10 ml THF. All components of the reaction mixture were soluble. An aliquot of the reaction mixture was used for the ^{31}P NMR spectrum: 2 resonances (δ), -21.73(s) and -40.29(s). For comparison, THF solutions of the various components had ^{31}P NMR resonances at -21.38 ($\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}$), -8.32 (KPPh_2) and 31.21 ($\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$). The literature value¹³ for PPh_2H is -41.1 ppm.

A ^1H NMR spectrum of a d^8 -THF solution of a reaction mixture prepared from 0.170 g (0.449 mmol) $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$, 0.101 g (0.451 mmol) KPPh_2 and 5 ml THF exhibited one pair of lines for the PH protons at δ 5.12 ppm, $J = 218$ Hz. For comparison, THF solutions of PPh_2H and $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ exhibited PH lines at δ 5.14 (d, $J = 218$ Hz) and 6.53, (d, 356 Hz), respectively.

Synthesis of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$. The complex, $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$, was prepared by the reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K} \cdot 2(\text{dioxane})$ with AlBr_3 in THF. The solvent, THF (20 mL), was distilled into a 2-neck flask containing 2.54 g (4.27 mmol) $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K} \cdot 2(\text{dioxane})$ and equipped with an addition tube containing 1.14 g (4.27 mmol) AlBr_3 . The AlBr_3 was added to the stirred suspension and immediate reaction occurred producing a white precipitate and an orange solution. The reaction mixture was stirred for 18 h and then THF was removed on the vacuum line leaving a very fluffy yellow solid. The reaction mixture was extracted several times with toluene (15 mL) to leave an insoluble white precipitate which was identified as KBr by qualitative tests for halogen and potassium. Its weight (0.506 g) corresponded to a 98.8% yield. The removal of the toluene from the solution produced a very sticky, dark yellow glass. Washing once with 10 mL hexane followed by fast removal of solvent gave 2.56 g (94%) of the compound identified as $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$, a fluffy, glassy brown-yellow solid. Mp: 55-63° glass forms, 68-70° glass melts with bubbling. Anal. Calc: C, 39.65; H, 2.85; Br, 25.12. Found: C, 40.52; H, 3.41; Br, 24.69. Analysis for bromine was performed on a sample hydrolyzed by an acetone/THF/water mixture. Normal

hydrolysis with dilute nitric acid gave a green solution, presumably containing Cr^{+3} . Addition of 5% AgNO_3 solution gave a clear solution and a black precipitate. ^1H NMR (d^8 -toluene, δ): 7.51(m, Ph), 7.24 (m, Ph), 3.18 (m, OCH_2), 1.58 (m, b, other CH_2). (The signal due to the residual methyl protons in d^8 -toluene at 2.31 was strong, possibly overlapping with the expected PCH_2 signal.) ^{31}P NMR (d^8 -toluene, ppm from 85% H_3PO_4 , δ): +72.6(s). IR (Nujol mull, cm^{-1}): 2071(m), 1975(m), 1938(vs). Cryoscopic molecular weight. Formula weight $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$: 636.1. Molality, obs. mol. wt., association: 0.0699, 929, 1.46; 0.0566, 992, 1.56; 0.0350, 770, 1.21. Solubility: very slightly soluble in hexane, moderately soluble in toluene or diethyl ether and soluble in THF. This compound exhibited very unusual behavior in hexane. Though it has low solubility in this solvent, $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$ swells in hexane. Fast removal of hexane produced a fluffy material that fills a large percent of the flask volume. Slow removal of hexane yielded a tenacious glass which was impossible to quantitatively remove from glassware using spatulas. The fluffy material slowly reverts to the tenacious glass with storage. This process can be slowed considerably by grinding the fluffy material to a fine powder. The fluffy material can be regenerated from the glass by adding hexane and then quickly removing it by vacuum distillation.

Synthesis of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$).

The series of compounds, $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$, were prepared from the reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2 \cdot 2(\text{dioxane})$ with dialkylaluminum bromides in THF. A specially constructed reaction vessel was used

to minimize contact of the reaction mixtures with high vacuum greases. It consisted of a 100 ml round bottom flask with a built-in addition tube which was separated from the flask by a Teflon valve, a constricted side-arm with an inner 14/35 joint, and an arm which allowed attachment to a vacuum system or to other apparatuses through a Teflon valve. The same procedure was followed for the preparations of these three compounds. In the dry-box, a hexane or toluene solution of the dialkylaluminum bromide (3-8 mmol in 2-5 mL solvent) was prepared in the built-in addition tube. A slight excess of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ was added to the flask through the 14/35 joint of the constricted side arm. The flask was evacuated and 40-50 mL THF was vacuum distilled into the flask. The constriction was washed of any $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$, the flask was cooled to -196° and sealed at the constriction. The dialkylaluminum bromide solution was added to the stirred $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ suspension at -78° . Immediate darkening of the reaction mixture was observed. The reaction mixture was slowly warmed to room temperature by allowing the dry ice in the -78° bath (contained in a large beaker) to evaporate (2-3 h). At this point, a brown-yellow solution and a white precipitate were present. Stirring was continued at room temperature for 12-15 h. The THF was removed by vacuum distillation and the reaction mixture was extracted twice with toluene (50 mL). The insoluble fraction, a light yellow solid, was identified as a mixture of KBr and unreacted phosphide complex by qualitative tests and infrared spectra. (In reactions where 1:1 molar ratios of reagents were used ($\text{R} = \text{Et}, \text{CH}_2\text{SiMe}_3$), a white solid was obtained, corresponding to a 95% yield of KBr.) After removal of

toluene, the resultant glass (R = Me) or solid (R = Et or CH₂SiMe₃) was purified as described in the following paragraphs.

The compound Cr(CO)₅[PPh₂(CH₂)₄OAlMe₂] was obtained as a brown-yellow glassy solid in 83.9% yield from the reaction of 2.15 g (3.62 mmol) Cr(CO)₅PPh₂K·2(dioxane) and 0.34 mL (0.47 g, 3.4 mmol) AlMe₂Br in THF. The product was purified by washing several times with hexane. Cr(CO)₅[PPh₂(CH₂)₄OAlMe₂] is soluble in ethers and aromatic hydrocarbons and is slightly soluble in hexane. It swells in hexane and undergoes the same reversible glass to fluffy solid behavior as the bromide analog. Mp: glass forms at 48-50°, 70° glass melts with bubbling. Anal. Calc.: C, 54.55; H, 4.77; P, 6.12; MeH, 2.00 moles/mole. Found: C, 56.46; H, 4.46; P, 5.95; MeH, 1.98 moles/mole. ¹H NMR (d⁸-toluene, δ): 7.74 (m, Ph), 7.44 (m, Ph), 3.84 (m, b, OCH₂), 2.31 (m, PCH₂), 1.51 (m, b, other CH₂), -0.64 (s, AlCH₃); integration OCH₂ to AlCH₃:1/3. IR (Nujol mull, cm⁻¹): ν_{CO} 2070(m), 1973(m), 1929(vs).

The reaction of 3.78 g (6.36 mmol) Cr(CO)₅PPh₂K·2(dioxane) and 0.81 mL (1.0 g, 6.3 mmol) AlEt₂Br in THF produced Cr(CO)₅[PPh₂(CH₂)₄OAlEt₂] as a tan solid in 55.9% yield. The product was purified by washing with hexane at -20°. It is slightly soluble in hexane and soluble in aromatic hydrocarbons and ethers. Mp: 159-160° with some decomposition. Anal. Calc.: C, 55.96; H, 5.26; P, 5.77; EtH, 2.00 moles/mole. Found: C, 50.71; H, 4.46; P, 5.97; EtH, 1.97 moles/mole. ¹H NMR (d⁸-toluene, δ): 7.74 (m, Ph), 7.48 (m, Ph), 3.68 (m, OCH₂), 2.47 (m, PCH₂), 1.62 (m, b, other CH₂), 1.26 (t, J = 8 Hz, CH₃), 0.10 (q, J = 8 Hz, AlCH₂); integration O-CH₂ to AlCH₂:1/2. ³¹P NMR (d⁸-toluene, ppm from 85% H₃PO₄, δ): +81.1(s). IR (Nujol mull, cm⁻¹): ν_{CO} 2067(m), 1972(m,sh), 1918(vs,b). Cryoscopic molecular

weight. Formula weight $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlEt}_2]$: 536.4 Molality, obs. mol. wt., association: 0.0638, 1050, 1.95; 0.0352, 853, 1.59.

The compound $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$ was obtained in 72.3% yield from the reaction of 3.25 g (5.47 mmol) $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ and 1.34 mL (1.45 g, 5.14 mmol) $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ in THF. The compound was obtained as a tan solid and was purified by crystallization from hexane or by washing with hexane at -20° . It has moderate solubility in hexane and good solubility in aromatic hydrocarbons and ethers. Mp: $100-101^\circ$. Anal. Calc.: C, 53.52; H, 6.19; P, 4.76; Me_4Si , 2.00 moles/mole. Found: C, 50.40; H, 5.77; P, 4.78; Me_4Si , 1.98 moles/mole. ^1H NMR (d^8 -toluene, δ): 7.69 (m, Ph), 7.35 (m, Ph), 3.89 (t, $J = 7$ Hz, OCH_2), 2.54 (m, b, PCH_2), 1.95 (m, CH_2), 1.53 (m, CH_2), 0.41 (s, AlCH_2), 0.29 (s, SiCH_3), 0.12 (s, SiCH_3), -0.69 (s, AlCH_2); integration $\text{OCH}_2/\text{all aluminum } \text{CH}_2\text{SiMe}_3$: 1/11. IR (Nujol mull, cm^{-1}): ν_{CO} 2070(m), 1973(m,sh), 1924(vs). Cryoscopic molecular weight. Formula weight $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$: 650.8. Molality, obs. mol. wt., association: 0.0682, 794, 1.22; 0.0373, 683, 1.05; 0.0307, 657, 1.01. Crystals suitable for x-ray diffraction were obtained by slow evaporation of solvent from a hexane solution using a greaseless recrystallization apparatus under the most strict anaerobic conditions, Mp: $102.5-103^\circ$. IR (Nujol mull, cm^{-1}): ν_{CO} 2070(m), 1972(m,sh), 1924(vs).

Collection of the X-Ray Diffraction Data. A number of crystals were sealed into thin-walled capillaries in an argon-filled dry-box and were examined by x-ray diffraction procedures. All were thin and of rather poor quality, with a "greasy" appearance and all gave diffraction

patterns with very few discernable data beyond $2\theta = 35^\circ$ ($\text{MoK}\alpha$). The best such crystal (dimensions $0.3 \times 0.3 \times 0.07$ mm) was selected for data collection. This was mounted on a Syntex P2₁ automated four-circle diffractometer. The crystal was centered accurately. Unit cell parameters and the orientation matrix were determined; data collection was carried out using a coupled $2\theta(\text{counter})-\theta(\text{crystal})$ scan. The method has been described previously;¹⁴ details appear in Table I. Data were corrected for absorption, and for Lorentz and polarization factors and were reduced to $|F_o|$ values. Any reflection with $I(\text{net}) < 0$ was assigned a value of $|F_o| = 0$.

Solution and Refinement of the Structure. All calculations were performed using our in-house Syntex XTL interactive structure determination system¹⁵ as modified at SUNY-Buffalo. The analytical form of the scattering factors of the appropriate neutral atoms were corrected for both the real ($\Delta f'$) and the imaginary ($i\Delta f''$) components of anomalous dispersion.¹⁶ The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$, where the weights were obtained from counting statistics modified by an "ignorance factor" (p) of 0.02.

The position of the chromium atom was quickly and unequivocally determined from an unsharpened three-dimensional Patterson synthesis. All other non-hydrogen atoms were located via a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. All hydrogen atoms (other than those of the methyl groups, which are indeterminate) were included in calculated positions based upon $d(\text{C-H}) = 0.95 \text{ \AA}$,¹⁷ $B = 6.0 \text{ \AA}^2$, and the appropriate idealized trigonal or tetrahedral geometry. Full matrix least-square refinement of positional parameters for all non-hydrogen atoms, anisotropic thermal

parameters for the heavier atoms (Cr,P,Si,Al) and isotropic thermal parameters for the lighter atoms, (O,C) led to final convergence ($(\Delta/\sigma)_{\max} < 0.1$) with $R_F = 9.2\%$, $R_{WF} = 8.2\%$ and $GOF = 1.82^{18}$ for 186 variables refined against those 1515 reflections with $|F_o| > 3\sigma(|F_o|)$. $[R_F = 7.4\%$, $R_{WF} = 7.6\%$ for those 1226 reflections with $|F_o| > 5\sigma(|F_o|)]$.¹⁹

A final difference-Fourier map showed no significant features (highest peak $0.54 \text{ e}\text{\AA}^{-3}$); the structure is thus complete. Final positional parameters appear in Table II. Calculated hydrogen atom positions (Table II-S) and anisotropic thermal parameters (Table III-S) have been deposited as Supplementary Material along with a list of observed and calculated structure factor amplitudes.

Reactions of $\text{Mo}(\text{CO})_5\text{PPh}_2\text{K}\cdot\text{dioxane}$ and $\text{W}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with AlBr_3 or AlEt_2Br in THF. The reactions of the molybdenum and tungsten carbonyl phosphide anions with AlBr_3 or AlEt_2Br were studied using the same procedure as described for $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$. These reactions were complicated by several factors. The solubility of both the metal carbonyl phosphide anions and the resultant products is lower than for the chromium derivatives. These properties lead to slower reactions and necessitated more numerous extractions for product isolation. Competing reactions, as evidenced by the presence of brown and black materials were observed. Characterization data for the products of these reactions is summarized below. Yields are given for reaction on a 2 mmol scale and assuming the product is $\text{M}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$.

$\text{Mo(CO)}_5\text{PPh}_2\text{K}\cdot\text{dioxane} + \text{AlBr}_3$. Brick-red solid (50%). Mp: decomposition begins at 140° . IR (Nujol mull, cm^{-1}): ν_{CO} 2080(vw), 2041(m), 1992(m), 1976(m), 1940(vs), 1891(m).

$\text{Mo(CO)}_5\text{PPh}_2\text{K}\cdot\text{dioxane} + \text{AlEt}_2\text{Br}$. Brown oil. IR (Nujol mull, cm^{-1}): ν_{CO} 2046(m), 1980(m), 1920(vs,b). Some carbon monoxide was generated by this reaction.

$\text{W(CO)}_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane}) + \text{AlBr}_3$. Red solid (73%). Mp: glass forms at 50° , melts to a bubbly liquid at 85° . IR (Nujol mull, cm^{-1}): ν_{CO} 2078(m), 2000(m), 1968(m), 1934(vs).

$\text{W(CO)}_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane}) + \text{AlEt}_2\text{Br}$. Yellow solid (25%, recrystallized from Et_2O). Mp: $110\text{--}115^\circ$. ^1H NMR (d^8 -toluene, δ): 7.52 (q, $J = 8$ Hz, Ph), 7.85 (m, Ph), 7.45 (m, Ph), 3.80 (m, OCH_2), 1.18 (m, other CH_2), 1.14 (t, $J = 7$ Hz, AlCH_2CH_3), 0.01 (q with further splitting, $J = 7$ Hz, AlCH_2). The compound had a low solubility in toluene. The spectral data were observed for a saturated d^8 -toluene solution but the strongest absorptions were those of the residual protons in the solvent. IR (Nujol mull, cm^{-1}): ν_{CO} 2060(m), 2035(w), 1985(m), 1910(vs,vb), 1823(m,sh).

Reactions of $\text{Cr(CO)}_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with Dialkylaluminum Bromides in Diethyl Ether and Dimethoxyethane. All of the following reactions were investigated using the same experimental procedure as previously described for THF.

Diethyl ether [AlEt_2Br]. The reaction of 0.35 mL (0.45 g, 2.7 mmol) AlEt_2Br with 1.713 g (2.88 mmol) $\text{Cr(CO)}_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ in 70 mL diethyl ether occurred slowly at room temperature. After 24 h a considerable quantity of an insoluble yellow solid, presumably $\text{Cr(CO)}_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$,

remained. The ether was removed by vacuum distillation and then the reaction mixture was extracted twice with 50 ml toluene. The yellow toluene insoluble solid (1.04 g) inflamed in air. Removal of toluene from the solution and then washing the resultant sticky solid with 10 ml hexane produced 0.740 g of a tan solid. All data suggest that the tan solid is $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlEt}_2\cdot\text{OEt}_2]$. Mp: 80° to a bubbly liquid. Anal. Calc.: EtH, 2.00 mol/mol. Found: 2.01 mol/mol. ^1H NMR (benzene, δ): 3.30 (s, OCH_2), 1.27 (t, $J = 8$ Hz, AlCH_2CH_3), 1.19 (m, OCH_2CH_3), 9.82 (q, $J = 8$, AlCH_2), integration. AlCH_2 : 1/1. IR (Nujol mull, cm^{-1}): 2072 (m), 1964 (m, sh), 1934 (s).

Diethylether [$\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$]. The reaction of 1.00 g (1.68 mmol) $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with 0.44 mL (0.41 g, 1.55 mmol) $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ in 50 mL diethylether appeared slower than the analogous reaction with AlEt_2Br . Work up of the reaction mixture was identical to the AlEt_2Br reaction and 0.45 g of a yellow, toluene insoluble, pyrophoric solid was isolated. The toluene soluble material, presumably impure $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlCH}_2\text{SiMe}_3)_2\cdot\text{OEt}_2]$, was a viscous brown oil and was characterized by ^1H NMR and IR. ^1H NMR (benzene, δ): 3.77 (s, b, OCH_2), 1.43 (d, b, OCH_2CH_3), 0.46 (s, SiMe), 0.32 (s, SiMe), 0.16 (s, SiMe), -0.49 (s, AlCH_2), -0.57 (s, AlCH_2), -0.67 (s, AlCH_2), integration $\text{OCH}_2/\text{AlCH}_2$: 17/20. The lowest field absorptions of both SiMe and AlCH_2 protons was much more intense than the higher field absorptions. IR (Nujol mull, cm^{-1}) 2078 (m), 2000 (w), 2974 (m), 1934 (vs).

Dimethoxyethane. The reaction of AlR_2Br ($\text{R} = \text{Et}, \text{CH}_2\text{SiMe}_3$) with $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ in DME was incomplete after 12-15 h but ^1H NMR spectral data for the products were consistent with the occurrence of

ether cleavage. The apparent products were sticky brown oils. ^1H NMR (benzene, δ): R = Et, 3.47 (s, b, OCH_3 and OCH_2), 2.29 - 0.98 (at least 13 lines, AlCH_2CH_3 and other alkyl absorbances), 0.31 (unsymmetrical sextet, $J = 8$ Hz, AlCH_2); R = CH_2SiMe_3 , 3.52 (m, b, OCH_2 and OCH_3), 1.52 (s, b), 1.11 (m, b), 0.48 (m, b, AlCH_2), 0.19 (s, SiMe).

Reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ with AlMe_3 . A 0.0408 g (0.5570 mmol) sample of AlMe_3 was distilled into a trap on the vacuum line. The complex, $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ (0.107 g, 0.283 mmol), was placed into a bulb equipped with a ^1H NMR tube side arm. Cyclopentane (0.4 mL) followed by the preweighed AlMe_3 were vacuum distilled into the bulb. The resulting solution was poured into the NMR tube and the tube (-196°) was sealed. The ^1H NMR spectrum was recorded over a period of twenty days and no change was observed. In a similar fashion, a d^8 -toluene solution of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and AlMe_3 was prepared. After several days at room temperature no change in the ^1H NMR spectrum was observed. This sample was heated at 140° for 14 h. The solution changed from pale yellow to dark yellow. Some changes were observed in the ^1H NMR spectrum of this solution and are discussed in the Results and Discussion Section.

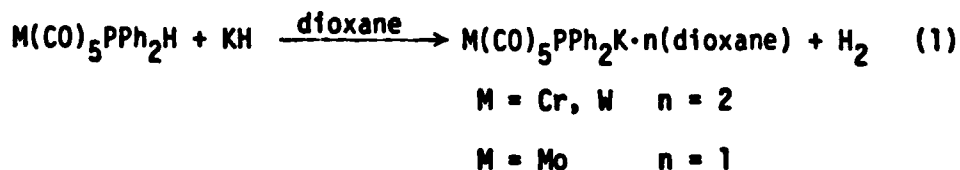
Reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ with AlMe_2H . A 0.0512 g (0.882 mmol) sample of AlMe_2H , followed by 2 mL hexane were vacuum distilled into a tube equipped with a Teflon stopcock. Hexane (8 mL) was vacuum distilled into a 2-neck flask which was fitted with the tube containing the alane solution and contained 0.3348 g (0.885 mmol) $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$. The two solutions were mixed and the reaction mixture changed from almost colorless to light yellow (0.5 h), to light brown (3 h), and

finally to grey brown over a 24 h period. A small amount (0.14 mmol) of an unidentified noncondensable gas was evolved. The volatile components were removed by vacuum distillation leaving a sticky light grey solid. Hydrolysis of the volatile components produced 0.426 mmol of a mixture of hydrogen and methane, corresponding to 0.142 mmol (16.1%) AlMe_2H . The infrared spectrum of a Nujol mull of the solid in the $2300\text{--}1500\text{ cm}^{-1}$ region had bands at 2259(w), 2224(w), 2160(w), 2078(m), 1974(m), 1931(vs), 1900(s,sh), 1523(w).

Results and Discussion

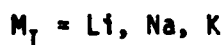
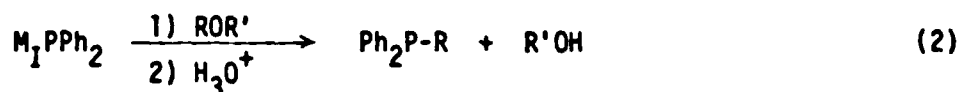
The syntheses of transition metal derivatives of amphoteric aluminum-phosphorus ligands have been investigated by starting with appropriate transition metal phosphorus complexes and then by attempting to form the desired Al-P bond. Transition metal phosphide anions would be expected to be ideal starting materials for metathetical reactions with aluminum halogen compounds. The deprotonation reactions of $M(CO)_5PPh_2H$ ($M=Cr, Mo, W$) with $n-BuLi$ in THF solution have been previously reported.³ However, potassium hydride has been described as a superior deprotonating reagent when compared with the more common reagents such as potassium metal,²⁰ $n-BuLi$ ^{20,21} and sodium or lithium hydride.²⁰ Furthermore, KH offers the preparative advantage that the extent of reaction can be easily monitored by measuring the evolved H_2 gas. Another important consideration is that KH does not react with the carbonyl ligands. Potassium hydride has been used to cleave metal-metal bonds in some transition metal carbonyl dimers to form the related metal anions and to deprotonate metal hydride cluster complexes without altering the carbonyl ligands.²²

The reaction of $M(CO)_5PPh_2H$ ($M=Cr, Mo, W$) with KH in dioxane produces quantitative yields of hydrogen and high isolated yields (>85%) of solid complexes of the general formula $M(CO)_5PPh_2K \cdot n(dioxane)$ - see equation 1. The reaction conditions involve the use of a slight

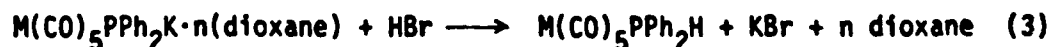


excess of $M(CO)_5PPh_2H$ which is easily removed from the product by extraction with hydrocarbon solvents. The low solubility of the potassium salts in ether solvents required pure KH and precluded the use of excess KH for preparative scale reactions. It is very difficult to separate KH from $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ unless very large quantities of solvent are employed. The compounds $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ are isolated as bright orange-yellow solids which do not melt but decompose on heating.

The presence of dioxane in $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ is easily deduced from the mass of the isolated product and confirmed by elemental analyses. These observations were cause for concern because uncomplexed alkali-metal phosphides cleave ethers²³ as described in equation 2. The integrity



of the bound dioxane molecules in $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ is demonstrated by reacting these complexes with anhydrous HCl or HBr in deuterated benzene or toluene - see equation 3. In all cases a pale yellow or pale orange solution and a colorless precipitate are formed. The 1H NMR spectra of these solutions indicate that ether cleavage does not occur and integration of the spectra give an estimate of the number of bound dioxane molecules. This experimental method has also been used to show that the phosphido



complexes can be stored in a dry-box for at least several months with no degradation of the dioxane. Similar experiments have demonstrated that only monosubstituted complexes are formed. Further confirmation of the

nature of the complexes was obtained by infrared data. However, solution spectra have not been obtained without observing extensive decomposition. The compounds exhibit an extreme sensitivity to air and water in ether solutions. In contrast, infrared spectra of Nujol mulls can be obtained without decomposition of the sample. In the case of $\text{Mo(CO)}_5\text{PPh}_2\text{K}\cdot\text{dioxane}$ and several other complexes to be discussed later, bands suggestive of a disubstituted complex are observed. However, these additional bands appear to be due to solid state effects because the carbonyl region of the infrared spectrum of the products of $\text{Mo(CO)}_5\text{PPh}_2\cdot\text{dioxane-HBr}$ reaction shows only the bands of $\text{Mo(CO)}_5\text{PPh}_2\text{H}$.

The ease of the deprotonation of $\text{M(CO)}_5\text{PPh}_2\text{H}$ with alkali metal hydrides depends on the nature of the solvent and metal hydride. KH is reactive in dioxane, THF and diethylether but not in hydrocarbon solvents. The chromium and molybdenum complexes from the reactions in THF are formulated as $\text{Cr(CO)}_5\text{PPh}_2\text{K}\cdot\text{THF}$ and $\text{Mo(CO)}_5\text{PPh}_2\text{K}\cdot\text{THF}$ on the basis of the products from the HCl reaction. The reactions of $\text{Cr(CO)}_5\text{PPh}_2\text{H}$ and $\text{W(CO)}_5\text{PPh}_2\text{H}$ with NaH have also been studied. These reactions are much slower than those with KH, requiring about one week at room temperature before hydrogen evolution ceases. Refluxing these reaction mixtures increases reaction rates but with reflux periods longer than 6-8 h undesirable red products form. Product purification is exceedingly difficult because $\text{M(CO)}_5\text{PPh}_2\text{Na}\cdot n(\text{ether})$, the red product and NaH exhibit little if any solubility in most solvents, including THF. Reactions of the sodium complexes with HBr show that the bound ether molecules are not cleaved and confirm monosubstitution. The long reaction times and the possibility of impure products severely limit the practical applications of the NaH reactions. The reactions of LiH with $\text{M(CO)}_5\text{PPh}_2\text{H}$

are even slower than those of NaH. In ether solvents, $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$ is best prepared by a previously published route.³ The reaction of LiEt_3H or lithium metal with $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ was incomplete. The use of LiAlH_4 results in destruction of the transition metal complex.

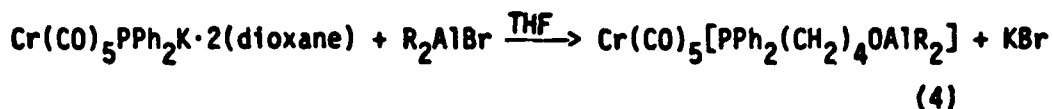
Attempts to prepare THF-free $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$ have met with limited success. It is not possible to completely remove THF from a solution of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$ (prepared³ from $n\text{-BuLi}$ and $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$) by high vacuum distillation, and heating the resultant glassy yellow material to $40\text{-}50^\circ$ leads to decomposition. Consequently, the deprotonation of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ with $n\text{-BuLi}$ in hydrocarbon solvents has been investigated. Addition of $n\text{-BuLi}$ solution to a hexane or toluene solution of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ initially leads to the precipitation of a yellow solid, presumably $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$, but within a few minutes a brown precipitate also forms. If the reaction mixture is hydrolyzed, up to one-third of the initial quantity of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ cannot be isolated. A possible source of these brown compounds is attack by $n\text{-BuLi}$ on the carbon monoxide ligands. This may be indicated by the infrared spectrum of impure $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$ which shows a weak band at 1658 cm^{-1} . This type of reaction is known for carbonyl compounds $\text{M}(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}, \text{PR}_3$) and produces carbene complexes.²⁴ The observation that the brown solids do not form until considerable $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$ has precipitated suggests that the carbonyl groups of this species rather than those of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ are being attacked. The quantity of the brown precipitate can be minimized by exceedingly slow addition of $n\text{-BuLi}$ solution to an excess of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ at room temperature. At the end of the reaction, $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$ is separated from unreacted $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ by filtration. The complex $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$ is extremely sensitive to oxygen and appears to be thermally unstable. This solid is much less stable than its THF solutions.

It is interesting to compare the infrared spectral properties of $M(CO)_5PPh_2K \cdot n(ether)$ with those of related compounds. The idea³ has been advanced that the carbonyl stretching frequencies of $M(CO)_5PPh_2Li$ ($M = Cr, Mo, W$) in THF solution are about 30 cm^{-1} lower than those of $M(CO)_5PPh_2H$ due to the partial delocalization of the charge on the phosphorus back to the metal and, in turn, to the π^* orbitals of the carbonyls. However, a comparison of the structural changes²⁵ within the series $Cr(CO)_5(XPh_3)$ ($X = P, As, Sb$) by x-ray structural studies are not compatible with the expectations for $Cr-X\text{ }d_{\pi}-d_{\pi}$ bonding. The picture is further confused by the observation that there is no significant difference between the frequencies of $M(CO)_5P(C_6F_5)_2Li$ and $M(CO)_5P(C_6F_5)_2H$ ($M = Cr, Mo$) in chloroform solution.²⁶ The choice of chloroform as solvent for these spectra has been questioned³ because $M(CO)_5PPh_2Li$ reacts with halogenated solvents. The compounds described in the current investigation also react with halogenated solvents. However, our data suggest the decrease in carbonyl stretching frequencies previously observed may be related to the presence of THF as a medium effect rather than a measure of charge delocalization onto the transition metal. The complexes described herein show the large decrease in frequency ($< 30\text{ cm}^{-1}$) in the high frequency band, as previously reported,³ but only when THF is tied up in the complex or present as the solvent. No regular pattern of decreased frequencies is observed for the other bands. It should be noted that delocalization of the negative charge on phosphorus need not occur solely to the transition metal. The significantly lower basicity of the uncomplexed diphenylphosphides M_1PPh_2 ($M_1 = Li, Na, K$) with respect to the alkyl or hydrido substituted phosphides has been attributed to the ability of the phenyl rings to delocalize the negative charge of the phosphorus.²³ Fluorination of the phenyl rings would be

expected to increase their ability to delocalize this charge. It seems possible that the perfluorinated rings could withdraw charge from the phosphorus, reduce its nucleophilicity so that $M(CO)_5\dot{P}(C_6F_5)_2Li$ may possess stability in halogenated solvents.

A preliminary examination of the basicity of $Cr(CO)_5PPh_2K$ relative to uncomplexed $KPPh_2$ toward the proton has provided both surprising and confusing results. When THF is the reaction solvent, ^{31}P and 1H NMR spectra of the solutions (all components are soluble) prepared by combining equimolar quantities of $Cr(CO)_5PPh_2H$ and $KPPh_2$ suggest that $KPPh_2$ is a significantly stronger base than $Cr(CO)_5PPh_2K$. The data including chemical shifts and coupling constants indicate that $Cr(CO)_5PPh_2H$ might have been deprotonated quantitatively. In contrast when diethyl ether is the reaction medium, the two anionic phosphides ($Cr(CO)_5PPh_2K$ and $KPPh_2$) which are both essentially insoluble in diethyl ether, exhibit similar basicities toward the proton. The soluble components of a reaction mixture produced by combining equimolar quantities of $KPPh_2 \cdot 2(\text{dioxane})$ and $Cr(CO)_5PPh_2H$ contain $Cr(CO)_5PPh_2H$ and PPh_2H in a 4:3 ratio. The reactions of solutions of $Fe(CO)_4PPh_2H$ with $LiPPh_2$ in THF^3 and solutions of $Mo(CO)_5PH_3$ with $KPPh_2$ in dimethyl ether²⁷ quantitatively produce the deprotonated transition-metal complex and the free phosphine. It is difficult to ascribe these differences to any one factor as the alkali-metal cation, the transition metal, the substituents on phosphorus, the solvent and the solubilities of all components could be involved in determining the position of the equilibrium. The solvent THF with its good solvating ability might also render an apparent leveling effect on the equilibrium.

The metathetical reactions of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with R_2AlBr ($\text{R}=\text{Br}, \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$) in THF at -78° have yielded compounds of the general formula²⁸ $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ and KBr in 95-99% yields based on equation (4). The reaction chemistry and ^1H NMR spectra



of the aluminum products indicate that the $(\text{CH}_2)_4\text{O}$ unit is a cleaved THF molecule as opposed to a simple THF adduct. This conclusion has also been substantiated by an x-ray structural study of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$. For example, attempts to displace the $(\text{CH}_2)_4\text{O}$ unit by Lewis bases such as NMe_3 and CH_3CN have resulted in the evolution of CO instead of loss of THF. Hydrolysis reactions have failed to produce compounds with P-H bonds as would be expected for compounds with P-Al bonds.⁹ The ^1H NMR spectra of all $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ compounds exhibit a broad absorption as an almost unbroken band in the range 2.5-1.0. The chemical shifts are consistent with the presence of oxygen and phosphorus bound methylene groups and alkyl residues but the broadness of the signals makes it difficult to propose a structure solely on the basis of ^1H NMR data. Further details of the ^1H NMR spectra of these compounds are discussed later. It is also significant that the chemical shifts of the lines in the ^{31}P NMR spectra of the bromo and ethyl derivatives are similar to those reported for $\text{Cr}(\text{CO})_5\text{PPh}_2\text{R}$ (R = various alkyl groups²⁹).

The x-ray structural study of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$ reveals that the crystal is composed of dimeric units which result,

in part, from the cleavage of C-O bonds in tetrahydrofuran, thereby producing P-[(CH₂)₄-O]-Al bridges.

There are no abnormally short intermolecular contacts. Indeed, as can quickly be seen from Figure 1, the structure is rather open with an appreciable amount of unutilized space. Labeling of atoms in the structure is shown in Figure 2, while Figure 3 provides a stereoscopic view of the molecule. (Note that the dimeric molecule is centered about the inversion center at 1/2, 0, 1/2. Atoms in the basic asymmetric unit are labeled normally. Those in the other half of the molecule are labeled with a prime and their coordinates are related to those of the basic unit by the transformation [x',y',z'] = [1-x,-y,1-z].)

The (OC)₅Cr-P portion of the structure has approximate C_{4v} symmetry and lends itself easily to comparison with the corresponding fragments in (OC)₅Cr(PPh₃)³⁰ and (OC)₅Cr[PPh₂Al(CH₂SiMe₃)₂·NMe₃].¹ The four equatorial Cr-CO linkages in the present molecule range from 1.84(2)Å through 1.88(2)Å (average = 1.86[2]Å),³¹ whereas the axial Cr-CO linkage is significantly shorter with Cr-C(5) = 1.79(2)Å. Analogous values are 1.880[11]Å versus 1.845(4)Å for (OC)₅Cr(PPh₃) and 1.888[6]Å versus 1.847(4)Å for (OC)₅Cr[PPh₂Al(CH₂SiMe₃)₂·NMe₃]. In each case this results from the greater competition for d_π electron density between the mutually trans pairs of equatorial carbonyl groups and the concomitant lower bond order in the Cr-CO (equatorial) versus Cr-CO (axial) bonds.

The Cr-P bond length of 2.383(6)Å in the present molecule is substantially shorter than that of 2.422(1)Å in (OC)₅Cr(PPh₃) and

that of $2.482(1)\text{\AA}$ found in the $(\text{OC})_5\text{Cr}[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{NMe}_3]$ molecule. The P-Cr-CO angles are normal.

The angles about the tetrahedrally-coordinated phosphorus atom show a systematic distortion from T_d toward C_{3v} coordination geometry, with expanded Cr-P-C angles (Cr-P-C(6)) = $111(1)^\circ$, Cr-P-C(12) = $121(1)^\circ$ and Cr-P-C(18) = $116(1)^\circ$ and contracted C-P-C angles (C(6)-P-C(12) = $100(1)^\circ$, C(6)-P-C(18) = $104(1)^\circ$ and C(12)-P-C(18) = $101(1)^\circ$). The phosphorus-carbon bond lengths appear to be equivalent within the limits of experimental error with the phosphorus-carbon(sp^3) distance being only P-C(18) = $1.83(2)\text{\AA}$ as compared to the phosphorus-carbon(sp^2) linkages P-C(6) = $1.82(2)\text{\AA}$ and P-C(12) = $1.82(2)\text{\AA}$.

Each all-staggered, zig-zag $(\text{CH}_2)_4$ chain, which connects the $(\text{OC})_5\text{CrPPh}_2$ fragment to the central O-Al-O'-Al' ring, has the expected C(sp^3)-C(sp^3) distances, with C(18)-C(19) = $1.53(3)\text{\AA}$, C(19)-C(20) = $1.53(2)\text{\AA}$ and C(20)-C(21) = $1.52(3)\text{\AA}$. The C(21)-O(6) distance of $1.45(2)\text{\AA}$ corresponds to a normal single bond, while angles along the $\text{P}(\text{CH}_2)_4\text{O}$ chain are P-C(18)-C(19) = $113(1)^\circ$, C(18)-C(19)-C(20) = $113(1)^\circ$, C(19)-C(20)-C(21) = $112(1)^\circ$ and C(20)-C(21)-O(6) = $112(1)^\circ$.

The Al_2O_2 system lies about an inversion center and defines a strictly planar, four-membered ring in which Al-O(6) = Al'-O(6') = $1.84(1)\text{\AA}$ and Al'-O(6) = Al-O(6') = $1.86(1)\text{\AA}$. The O-Al-O angles are acute [O(6)-Al-O(6') = O(6')-Al'-O(6) = $79.7(5)^\circ$] while Al-O-Al angles are obtuse [Al-O(6)-Al' = Al'-O(6')-Al = $100.3(6)^\circ$] - consistent with an electron-precise species with no direct Al...Al' bonding. The geometry of this central Al_2O_2 system is rather similar to that found in the centrosymmetric dimeric species $[\text{Me}_3\text{SiOAlBr}_2]_2^{32}$ in which

$\text{Al-O} = 1.79(1)\text{--}1.80(1)\text{\AA}$, $\text{O-Al-O}' = 84.4(4)^\circ$ and $\text{Al-O-Al}' = 95.6(4)^\circ$.

The coordination environment about the ring oxygen atoms (O(6) and O(6')) is trigonal and close to planar, with $\text{Al-O(6)-Al}' = 100.3(6)^\circ$, $\text{Al-O(6)-C(21)} = 129.7(10)^\circ$, and $\text{Al}'\text{-O(6)-C(21)} = 128.1(10)^\circ$.

The aluminum atoms are each bonded to two oxygen atoms (vide supra) and to two (trimethylsilyl)methyl ligands with $\text{Al-C(22)} = 1.95(2)\text{\AA}$ and $\text{Al-C(26)} = 1.94(2)\text{\AA}$. The tetrahedral coordination environment of each aluminum atom is extremely irregular with $\text{O(6)-Al-O(6')} = 79.7(5)^\circ$, O-Al-C angles in the range $110.4(7)\text{--}113.6(7)^\circ$ and $\text{C(22)-Al-C(26)} = 121.5(8)^\circ$.

All other geometric features of the molecule are normal.

The nature of $\text{Cr(CO)}_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl(CH}_2\text{SiMe}_3)_2]$ in benzene solution has also been investigated. All data are consistent with the existence of a monomer-dimer equilibrium which is slow on the NMR time scale. Cryoscopic molecular weight data indicate that association varies from 1.01-1.22 in the concentration range 0.0307-0.0682 m. This low association also suggests that species more associated than dimers are probably not present in significant concentrations. The ^1H NMR spectrum of the compound in benzene solution exhibits two sets of two lines for the trimethylsilylmethyl protons which are concentration dependent and consistent with a slow monomer-dimer equilibrium. At the lowest concentration of 0.101 m, the monomeric species with chemical shifts of 0.42 (AlCH_2) and 0.12 (SiMe_3) and the dimeric species with chemical shifts 0.29 (SiMe_3) and -0.69 (AlCH_2) are present in approximately equal

concentrations. At a higher concentration of 0.305 m, the monomeric species has virtually disappeared. The large differences in chemical shifts for the aluminum methylene protons of 0.42 and -0.69 further support the identification of monomers and dimers. If more associated species such as dimers and trimers were present in solution instead of monomers and dimers, the chemical shifts of the lines would be expected to be similar. Furthermore, calculations of net association from ^1H NMR integrations and cryoscopic molecular weight data show a fairly regular transition from monomeric to dimeric association with increasing concentration. The possibility that the monomer exists as a chelated species with the aluminum bound to a carbonyl oxygen has not been investigated.

The ethyl derivative $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlEt}_2]$ is probably very similar in nature to the trimethylsilylmethyl compound in the solid phase and in solution. Both compounds can be crystallized and exhibit true melting point behavior. Cryoscopic molecular weight measurements in benzene solution also indicate that a monomer-dimer equilibrium exists but a larger percentage of the ethyl derivative exists as a dimer at similar concentrations. However, the ^1H NMR spectra of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlEt}_2]$ do not exhibit an apparent large concentration dependence at the concentrations studied but small effects can be observed. The individual lines due to the protons on the α -carbon of the ethyl group bound to aluminum are broader than those of the triplet for the protons on the β -carbon. This may indicate that the reactions of the equilibrium are faster than those for the more bulky trimethylsilylmethyl substituted derivative.

The reactions of AlMe_2Br and AlBr_3 with chromium-diphenylphosphide

anions in THF also yield products indicative of THF cleavage. Even though analytical²⁸ and ¹H NMR data indicate the general formula $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ (R=Me,Br), these compounds exhibit some unusual properties which suggest that their associations in the condensed phase are different from the CH_2SiMe_3 and C_2H_5 derivatives. The complexes $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlMe}_2]$ and $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$ are glasses at room temperature. They do not melt but undergo several phase transitions when heated. All attempts to crystallize these compounds have been unsuccessful. Fast removal of ether or hydrocarbon solvents under high vacuum from these complexes leaves a fluffy, airy, golden brown material. If the solvent is removed slowly a viscous glass remains. This phenomenon is independent of the solubility of the complex in the solvent. In a solvent such as hexane, in which these complexes have only very slight solubility, the fluffy glass form of these compounds immediately changes to the viscous glass on contact. The glass appears to swell with hexane. The glass can also be obtained by storing the fluffy solid for several days and this process can be reversed by adding a solvent and quickly removing it under vacuum. These types of behavior are indicative of changing association and are observed with noncrystalline polymers.³³ Cryoscopic molecular weight data of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$ in benzene solution suggest that a monomer-dimer equilibrium is present. However, the association did not vary in a regular fashion with concentration, possibly indicating that equilibrium is only slowly attained.

A fundamental question concerning the reaction of chromium

diphenylphosphide anions with aluminum halides to yield final products indicative of THF cleavage is whether a species with a Cr-P-Al atom sequence is initially formed. Subsequent reaction of $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlR}_2\cdot\text{THF}]$ by dissociation at the Al-P bond with formation of ion pairs followed by nucleophilic attack of a $\text{Cr}(\text{CO})_5\text{PPh}_2^-$ anion on a $\text{R}_2\text{Al}\cdot\text{THF}^+$ cation provides a reasonable pathway in the polar solvent THF. (Pathway 1). This pathway is consistent with our experimental observations. A "concerted" reaction of $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlR}_2\cdot\text{THF}]$ is also a possible route for THF cleavage (Pathway 2). If the Cr-P-Al atom sequence is not formed, then a $\text{R}_2\text{AlBr}\cdot\text{THF}$ adduct would have to undergo a nucleophilic attack by $\text{Cr}(\text{CO})_5\text{PPh}_2^-$ (Pathway 3). Based upon our current data, Pathway 1 is favored but a "concerted" process (Pathway 2) cannot be ruled out. The compound¹ $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{NMe}_3]$ reacts with THF at room temperature over 24 h to form $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{Al}(\text{CH}_2\text{SiMe}_3)_2]$. The observed long P-Al bond¹ in $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{NMe}_3]$ and its reaction chemistry with HBr suggest that dissociation at the Al-P bond to form ion pairs should be a facile process especially in THF solution. Another significant observation is that organoaluminum phosphides R_2AlPPh_2 ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$) cleave THF under mild conditions⁹ suggesting that THF cleavage is a facile process even in the absence of a transition metal. Our data suggest that dimethoxyethane can also be cleaved during reactions of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}$ with AlR_2Br ($\text{R} = \text{Et}, \text{CH}_2\text{SiMe}_3$). The spectral data for products from these reactions in DME are consistent with ether cleavage but pure products could not be isolated. In contrast to these observations, diethyl ether is not cleaved. The phosphide, $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$, reacts with $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ or AlEt_2Br in diethyl ether to give high yields of products whose spectral properties are consistent with the

formation of $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlR}_2\cdot\text{OEt}_2]$ ($\text{R} = \text{Et}, \text{CH}_2\text{SiMe}_3$). Pathway 3, nucleophilic attack of aluminum ether adduct by $\text{Cr}(\text{CO})_5\text{PPh}_2^-$ is considered the least likely. A preliminary study of a reaction mixture of 1 mol $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ and 1 mol AlMe_3 in THF indicates that only slight ether cleavage occurs after 3 days at room temperature.

The reactions of $\text{Mo}(\text{CO})_5\text{PPh}_2\text{K}\cdot\text{dioxane}$ and $\text{W}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with AlEt_2Br or AlBr_3 in THF have also been examined. Reactions of these molybdenum and tungsten complexes are much slower, the number of by-products is greater and the isolation of major products is more difficult than for the chromium complex. All of the factors are probably related to the lower solubility of the molybdenum and tungsten reactants and products. Available data suggest that with tungsten, complexes of simplest formula $\text{W}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ are isolated. The main products of the molybdenum reactions and the secondary products of the tungsten reactions appear to be disubstituted complexes.

A second possible route to transition metal derivatives of amphoteric-aluminum phosphorus ligands involves small molecule elimination reactions between $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and AlMe_3 or AlMe_2H , a common class of reaction in main-group chemistry.^{2,9,34} Methane or H_2 would be the expected small molecule products. Even though the chemistry of transition metal complexes of phosphines containing reactive substituents has been found to resemble that of the free phosphine,³⁵ the predicted elimination reaction with formation of the desired Al-P bond does not occur. The majority of the aluminum compound is consumed but most $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ does not react. These

observations suggest that the major site of reaction for the aluminum compound is the carbonyl ligand. Kinetic studies of related elimination reactions³⁶ suggest that the geometry of the transition state is very important in these types of reactions. The aluminum-phosphorus bond would be formed as the small molecule is being eliminated. Consequently, the existence of the Cr-P bond by use of the phosphorus lone pair in $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ precludes the necessary transition state for elimination.

It is interesting to compare and contrast our attempts to synthesize compounds of the type $\text{M}(\text{CO})_5[\text{PPh}_2\text{AlR}_2]$ with a study in which compounds of the type $\text{M}(\text{CO})_5[\text{PPh}_2\text{B}(\text{NR}_2)_2]$ were reported.³⁷ The boron-phosphorus compounds were obtained by the reaction of $\text{M}(\text{CO})_5\text{PPh}_2^-$ and $\text{B}(\text{NR}_2)_2\text{Br}$ in THF and the ligand displacement reactions of $\text{M}(\text{CO})_5\text{L}$ ($\text{L}=\text{CO}, \text{THF}, \text{CH}_3\text{CN}$) by $\text{B}(\text{NR}_2)_2\text{PR}_2$. The analogous reactions to produce the aluminum compounds have yielded compounds in which the Al-P bond is cleaved and the Al and P atoms are bound to first row elements instead. The only successful route to compounds of the type $\text{M}(\text{CO})_5[\text{PPh}_2\text{AlR}_2]$ has involved displacement of the relatively unreactive ligand NMe_3 of $\text{Cr}(\text{CO})_5\text{NMe}_3$ by $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$.

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Supplementary Material Available

A listing of observed and calculated structure factor amplitudes, calculated hydrogen atom parameters (Table II-S) and anisotropic thermal parameters (Table III-S) (15 pages).

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 $R_{WF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \times 100(\%)$;
 $GOF = [\sum w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$.

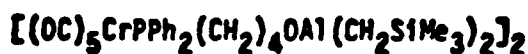
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$$[\sigma] = \left[\sum_{i=1}^{i=n} (d_i - \bar{d})^2 / (N-1) \right]^{1/2}.$$

Here d_i is the i^{th} and \bar{d} is the mean of N "equivalent" bond lengths or angles.
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Table 1.

Data for the X-Ray Diffraction Study of



(A) Crystal Parameters at 24°C^a

Crystal system:	monoclinic	$V, \text{\AA}^3$	3654
Space group:	$P2_1/n$	Z	2
$a, \text{\AA}$	11.939(3)	mol wt	1301.51
$b, \text{\AA}$	14.940(3)	$\rho(\text{calcd}), \text{g cm}^{-3}$	1.18
$c, \text{\AA}$	21.014(5)	ν, cm^{-1}	4.9
β, deg	102.88(2)		

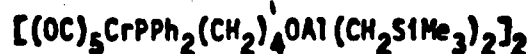
(B) Measurement of Intensity Data

diffractometer:	Syntex $P2_1$
radiation:	$\text{MoK}\alpha (\lambda 0.71073 \text{\AA})$
monochromator:	highly oriented graphite (equatorial mode)
reflections measured:	$+h, +k, \pm l$ for $4.0^\circ < 2\theta < 35.0^\circ$
scan type:	coupled $2\theta(\text{counter})-\theta(\text{crystal})$
scan speed:	3.0 deg min^{-1}
scan width:	symmetrical, $[2.0 + \Delta(\alpha_1 - \alpha_2)]^\circ$
background:	at beginning and end of scan, each for 1/2 scan time
reflections collected:	2491 total, yielding 2327 independent data; 1515 with $ F_o > 3.0\sigma(F_o)$
standards:	3 collected every 97 data; no significant variations.

^aBased on the setting angles of the unresolved $\text{MoK}\alpha$ components of 24 reflections of the forms $\{1,1,\overline{12}\}$, $\{1,10,1\}$, $\{6,2,\overline{3}\}$, $\{5,4,\overline{2}\}$, $\{4,3,\overline{10}\}$, $\{4,6,\overline{8}\}$.

Table II

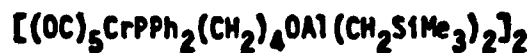
Positional Parameters for Non-Hydrogen Atoms in



ATOM	X	Y	Z	BISO
CR	0.61884(25)	0.46849(21)	0.38569(15)	
P	0.73965(42)	0.33172(32)	0.48235(24)	
S11	0.22453(56)	0.14678(46)	0.55758(32)	
S12	0.24818(53)	0.18281(39)	0.32288(31)	
AL	0.39439(46)	0.84483(48)	0.47512(27)	
O1	0.8238(12)	0.57939(87)	0.38537(68)	5.88(35)
O2	0.6558(11)	0.47911(85)	0.53142(68)	6.18(35)
O3	0.5798(12)	0.43468(91)	0.23993(74)	7.23(48)
O4	0.4887(12)	0.35636(91)	0.38522(63)	6.34(37)
O5	0.4818(13)	0.6285(11)	0.36956(78)	8.06(43)
O6	0.53669(88)	0.86689(68)	0.52833(58)	3.52(28)
C1	0.7445(17)	0.5316(14)	0.38437(88)	5.14(58)
C2	0.6485(15)	0.4726(12)	0.4747(18)	4.48(48)
C3	0.5968(16)	0.4473(14)	0.2954(11)	5.78(53)
C4	0.4858(17)	0.3956(13)	0.38837(91)	4.73(51)
C5	0.5361(20)	0.5611(16)	0.3761(11)	7.37(65)
C6	0.8835(14)	0.3578(11)	0.39231(83)	2.86(41)
C7	0.9637(16)	0.3911(12)	0.44282(87)	4.11(46)
C8	1.0742(16)	0.4225(13)	0.4322(18)	5.68(55)
C9	1.0921(16)	0.4162(12)	0.3695(11)	5.34(53)
C10	1.0123(18)	0.3823(13)	0.3194(18)	5.37(52)
C11	0.9871(15)	0.3536(11)	0.33122(87)	3.99(45)
C12	0.7876(16)	0.2334(12)	0.35849(85)	3.79(45)
C13	0.6835(18)	0.2238(13)	0.3867(18)	5.59(52)
C14	0.5884(18)	0.1461(15)	0.2653(18)	6.38(57)
C15	0.6626(20)	0.8842(14)	0.2727(18)	6.38(57)
C16	0.7631(20)	0.8872(14)	0.3179(11)	6.87(59)
C17	0.7853(16)	0.1647(15)	0.35641(93)	5.51(53)
C18	0.7649(14)	0.2885(11)	0.48319(79)	3.51(43)
C19	0.6579(15)	0.2342(12)	0.49667(84)	4.81(45)
C20	0.6816(14)	0.1846(11)	0.56289(79)	3.48(43)
C21	0.5743(16)	0.1384(12)	0.57377(85)	4.34(47)
C22	0.2736(15)	0.8438(13)	0.52391(85)	4.84(46)
C23	0.3821(17)	0.1649(13)	0.6474(18)	6.28(56)
C24	0.8668(21)	0.1446(16)	0.5535(12)	9.49(72)
C25	0.2546(17)	0.2585(14)	0.5182(18)	7.85(61)
C26	0.3742(14)	0.1857(12)	0.39165(84)	3.98(44)
C27	0.2482(20)	0.2838(15)	0.2642(11)	8.28(63)
C28	0.2464(19)	-0.8849(15)	0.2768(11)	8.26(68)
C29	0.1849(19)	0.1899(15)	0.3588(11)	8.25(67)

Table IV

Intramolecular Distances (Å) for



(A) Distances from the Chromium Atom

Cr-P	2.383(6)	Cr-C(3)	1.87(2)
Cr-C(1)	1.84(2)	Cr-C(4)	1.88(2)
Cr-C(2)	1.84(2)	Cr-C(5)	1.79(2)

(B) Distances within the Carbonyl Ligands

C(1)-O(1)	1.18(3)	C(4)-O(4)	1.15(3)
C(2)-O(2)	1.17(3)	C(5)-O(5)	1.19(3)
C(3)-O(3)	1.15(3)		

(C) Phosphorus-Carbon Distances

P-C(6)	1.82(2)	P-C(18)	1.83(2)
P-C(12)	1.82(2)		

(D) Distances within the $(CH_2)_4O$ Fragment

C(18)-C(19)	1.53(3)	C(20)-C(21)	1.52(3)
C(19)-C(20)	1.53(2)	C(21)-O(6)	1.45(2)

(E) Aluminum-Carbon and Aluminum-Oxygen Distances

Al-C(22)	1.95(2)	Al-O(6)	1.84(1)
Al-C(26)	1.94(2)	Al-O(6')	1.86(1)

(F) Silicon-Carbon Distances

Si(1)-C(22)	1.84(2)	Si(2)-C(26)	1.84(2)
Si(1)-C(23)	1.93(2)	Si(2)-C(27)	1.95(2)
Si(1)-C(24)	1.88(3)	Si(2)-C(28)	1.87(2)
Si(1)-C(25)	1.92(2)	Si(2)-C(29)	1.92(2)

(G) Carbon-Carbon Distances within Phenyl Rings

C(12)-C(13)	1.38(3)	C(6)-C(7)	1.36(3)
C(13)-C(14)	1.44(3)	C(7)-C(8)	1.46(3)
C(14)-C(15)	1.33(3)	C(8)-C(9)	1.38(4)
C(15)-C(16)	1.36(3)	C(9)-C(10)	1.35(3)
C(16)-C(17)	1.40(3)	C(10)-C(11)	1.40(3)
C(17)-C(12)	1.37(3)	C(11)-C(6)	1.38(3)

Table V.

Selected Angles (in Deg) within the

$[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$ Molecule

(A) Angles Around the Chromium Atom

C(1)-Cr-C(2)	91(1)	C(2)-Cr-P	89(1)
C(1)-Cr-C(3)	89(1)	C(3)-Cr-C(4)	93(1)
C(1)-Cr-C(4)	175(1)	C(3)-Cr-C(5)	91(1)
C(1)-Cr-C(5)	87(1)	C(3)-Cr-P	91(1)
C(1)-Cr-P	90(1)	C(4)-Cr-C(5)	89(1)
C(2)-Cr-C(3)	180(1)	C(4)-Cr-P	94(1)
C(2)-Cr-C(4)	87(1)	C(5)-Cr-P	176(1)
C(2)-Cr-C(5)	89(1)		

(B) Angles Around the Phosphorus Atom

Cr-P-C(6)	111(1)	C(6)-P-C(12)	100(1)
Cr-P-C(12)	121(1)	C(6)-P-C(18)	104(1)
Cr-P-C(18)	116(1)	C(12)-P-C(18)	101(1)

(C) Angles in the $(CH_2)_4O$ Fragment

P-C(18)-C(19)	113(1)	C(19)-C(20)-C(21)	112(1)
C(18)-C(19)-C(20)	113(1)	C(20)-C(21)-O(6)	112(1)

(D) Angles Around Aluminum Atom

O(6)-Al-O(6')	79.7(5)	O(6')-Al-C(22)	113.6(7)
O(6)-Al-C(22)	111.9(7)	O(6')-Al-C(26)	110.4(7)
O(6)-Al-C(26)	112.3(7)	C(22)-Al-C(26)	121.5(8)

(E) Angles Around O(6)

Al-O(6)-Al⁺ 100.3(6)

Al-O(6)-C(21) 129.7(10) Al⁺-O(6)-C(21) 128.1(10)

(F) Aluminum-Carbon-Silicon Angles

Al-C(22)-Si(1) 122.2(10) Al-C(26)-Si(2) 127.6(10)

(G) Angles Around Silicon Atoms

C(22)-Si(1)-C(23) 111.7(9) C(26)-Si(2)-C(27) 111.0(9)

C(22)-Si(1)-C(24) 111.9(10) C(26)-Si(2)-C(28) 111.5(9)

C(22)-Si(1)-C(25) 111.3(9) C(26)-Si(2)-C(29) 113.0(9)

C(23)-Si(1)-C(24) 107.8(10) C(27)-Si(2)-C(28) 109.2(10)

C(23)-Si(1)-C(25) 106.9(9) C(27)-Si(2)-C(29) 105.5(10)

C(24)-Si(1)-C(25) 107.1(10) C(28)-Si(2)-C(29) 107.6(10)

Captions to Figures

- Figure 1. Packing of molecules in crystalline $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$.
- Figure 2. Labeling of atoms in the $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$ molecule. All oxygen atoms are stippled; the molecular and crystallographic center of symmetry is marked with a saltire (x). [ORTEP-II diagram; 30% probability ellipsoids.]
- Figure 3. Stereoscopic view of the $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$ molecule.

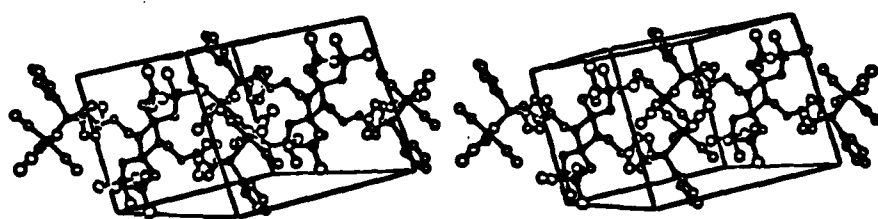


FIGURE 1

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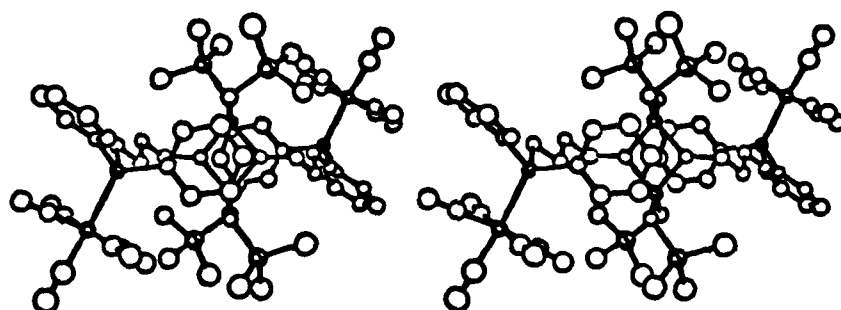


FIGURE 3
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